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## Calculations on Surface Double Layers in Alkali Halide Thin Films

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### Abstract

The surface double layer in a thin film is discussed in the framework of Kliewer and Koehler's theory for pure and impure Schottky-type ionic crystals. The method of numerical calculation to obtain the potential profile and the distribution of lattice defects in the thin film is outlined. It is found that charge neutrality is not maintained in all parts of crystal due to the excess positive ion vacancies existing all through the internal region in pure thin crystal.

### § 1 Introduction

It is well recognized that there exist Debye-Hückel clouds with their inherent electrostatic potential in the vicinity of such crystalline defects as dislocations, crystal subgrain boundaries, crystal surfaces, due to the difference in the formation energies of the constituent lattice defects. While charged dislocations have been rather widely investigated by the methods of the indentation pulse analyses,<sup>1)</sup> internal friction measurements<sup>2)</sup> and others, the properties of surface double layers are not well understood because of quite a few experimental difficulties such as atmosphere surrounding a crystal surface, surface treatments, etc. Studies on surface double layers in silver halides have been recently initiated by the Kodak group<sup>3)</sup> to find that the photographic properties of fine powders and thin films can be explained in terms of the presence of surface double layers.

Lehovec<sup>4)</sup> considered the problems on the crystal surface of ionic crystals to propose several prospective experiments on the basis of the presence of surface double layers. More detailed theoretical treatment has been worked out by Kliewer and Koehler<sup>5)</sup> and concurrently by Lifshitz and Geguzin.<sup>6)</sup> More realistic approach has been done by Poeppl and Blakely<sup>7)</sup> assuming that numbers of crystal defects generating out of a crystal surface are finite. These authors find theoretically and experimentally that a magnitude of static potential across a surface reduces rather rapidly due to an inability for a surface to generate lattice defects at high temperatures.

All these works do not deal with thin films the thickness of which are comparable to that of the surface double layer in bulk crystals. The purpose of the present paper is to discuss the behaviors of the surface double layer in thin films in case of pure and impure crystals. The main scheme of this work is essentially an extension of Kliewer and Koehler's theory.

## §2 The Method of Calculations and Results

Consider an ionic crystal with Schottky-type lattice defects. Let the formation energy of positive ion vacancy be smaller than that of negative ion vacancy as is the case of sodium chloride. Crystal thickness is taken to be  $2L$  and an extension of the crystal surface will be assumed to be infinite. In view of the geometrical symmetry of the crystal, we have only to deal with one half of the crystal thickness; by taking  $x$  axis vertical to the surface, the coordinate  $x$  ranges from 0 to  $L$ . One can determine the densities of positive ion vacancy  $n_+$  and of negative ion vacancy  $n_-$  as a function of  $x$ , such that they minimize the total Helmholtz free energy of the crystal and also they satisfy the Poission's equation with relevant boundary conditions.

### Pure Case

Helmholz free energy  $F$  is given by

$$F = \int_0^L dx \left[ n_+(x) F^+ + n_-(x) F^- + n_B(x) \{ F^+ + F^- - B \} + \frac{1}{2} \rho(x) \Phi(x) \right] - T S_c. \quad (1)$$

Here  $F^+$ ,  $F^-$  and  $B$  are, respectively, the formation energy of positive ion vacancy, that of negative ion vacancy and the binding energy of positive and negative ion vacancies.  $n_B$  indicates the density of neutral ion pairs.  $T$  and  $S_c$  are an absolute temperature and the configurational entropy of lattice defects, respectively. Charge density  $\rho(x)$  and an electrostatic potential  $\Phi(x)$  are related by the following equations:

$$\frac{d^2 \Phi(x)}{dx^2} = - \frac{4\pi}{\epsilon} \rho(x), \quad (2)$$

$$\rho(x) = e \{ n_-(x) - n_+(x) \}, \quad (3)$$

with the boundary conditions

$$\Phi(0) = 0, \quad (4)$$

$$\frac{d\Phi}{dx} = 0 \quad \text{at } x = L, \quad (5)$$

where  $\epsilon$  and  $e$  are dielectric constant of the crystal and an electronic charge, respectively. Minimizing  $F$  with respect to  $n_+$ , and  $n_-$  and  $n_B$  subject to the eq. (2) through eq. (5), one finds  $n_+$  and  $n_-$  as

$$n_+ = N \exp \left[ - \frac{F^+ - e\Phi(x)}{kT} \right], \quad (6)$$

$$n_- = N \exp \left[ - \frac{F^- + e\Phi(x)}{kT} \right]. \quad (7)$$

Here  $N$  is numbers of ions per unit volume,  $k$  Boltzmann constant,  $T$  an absolute temperature.

Substituting eq. (6) and eq. (7) to eq. (2) and eq. (3), we find  $\Phi(x)$  as a solution of Poisson's equation. In so doing, the following conversion of the variables are found to be useful;

$$z(x) = \frac{1}{kT} \{e\Phi(x) - e\Phi_\infty\}, \quad (8)$$

$$s = \kappa x, \quad (9)$$

where  $\Phi_\infty$  and  $\kappa$  are defined as follows;

$$\Phi_\infty = \frac{1}{2e} (F^+ - F^-), \quad (10)$$

$$\kappa = \left\{ \frac{8\pi N e^2}{\epsilon kT} \exp \left[ \frac{e\Phi_\infty - F^+}{kT} \right] \right\}^{1/2}. \quad (11)$$

Poisson's equation turns out to be simply, after the variable conversion,

$$\frac{d^2 z}{ds^2} = \sinh z. \quad (12)$$

Here let it be that

$$z_0 \equiv z|_{x=0} = -\frac{e\Phi_\infty}{kT}, \quad (13)$$

$$z_L \equiv z|_{x=L}. \quad (14)$$

The solution to eq. (12) is given as follows;

$$s = \zeta F \left( \sin^{-1} \left\{ \frac{\cosh z_0 - \cosh z_L}{\cosh z_0 - 1} \right\}, \zeta \right) - \zeta F \left( \sin^{-1} \left\{ \frac{\cosh z - \cosh z_L}{\cosh z_0 - 1} \right\}, \zeta \right), \quad (15)$$

where

$$\zeta = \sqrt{\frac{2}{1 + \cosh z_L}}. \quad (16)$$

$F(\sin^{-1} \left\{ \frac{\cosh z_0 - \cosh z_L}{\cosh z_0 - 1} \right\}, \zeta)$ ,  $F(\sin^{-1} \left\{ \frac{\cosh z - \cosh z_L}{\cosh z_0 - 1} \right\}, \zeta)$  in eq. (15) show the elliptic integrals of the first kind with the appropriate arguments. Eq. (15) can be written formally as

$$z = z(s; z_0, z_L). \quad (17)$$

Here  $z$  is a function of  $s$  with  $z_0, z_L$  as parameters. Noting that  $z_L$  must be between 0 and  $z_0$ , eq. (17) can be obtained numerically once the parameter  $z_0$  is fixed. Fig. 1 shows the results for  $z_0=1$ ,  $z_L=0.9, 0.7, 0.5, 0.3$ , and  $0.1$ . The point worth mentioning is that  $z_L=0.62$  for  $s=\kappa L=1$ , i.e.  $L \simeq \kappa^{-1}$ , which shows that thin film of an order of the thickness of surface double layer in a bulk crystal has its potential leveled up by 62% of the bulk crystal at midpoint. In other words, the static potential of such a film decreases gradually down

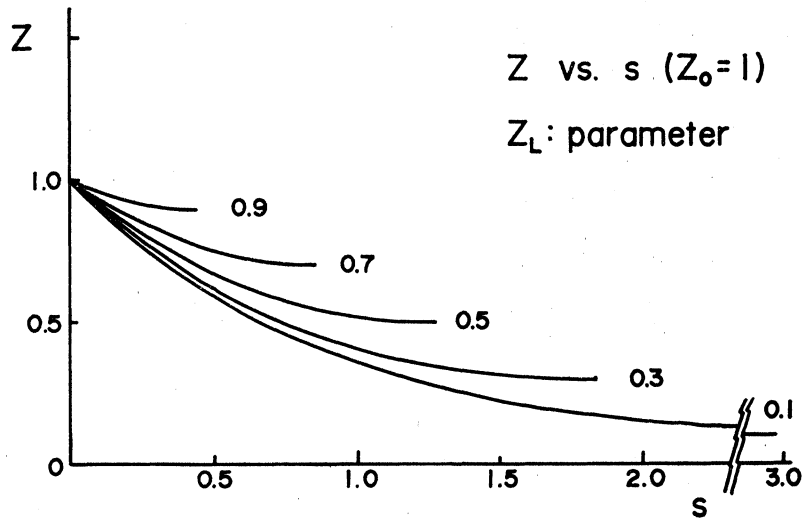


Fig. 1

to 62% of the value at the surface in crossing the thickness from the surface to the mid-point. With  $L$  increasing to  $\infty$ , the potential at  $x=L$  with respect to the crystal surface is of course  $z_0=-1=-e\phi_\infty/kT$  as it should be and the potential profile, that is  $\Phi(x)$  vs.  $x$  is in general represented by the curve with  $z_L=0.1$ . The density of positive ion vacancies  $n_+/N$  varies with  $x$  in analogy with  $z$  vs.  $s$  and there exist excess numbers of positive ion vacancies in clear contrast with the case of bulk crystal in which almost all parts of crystal maintain the charge neutrality.

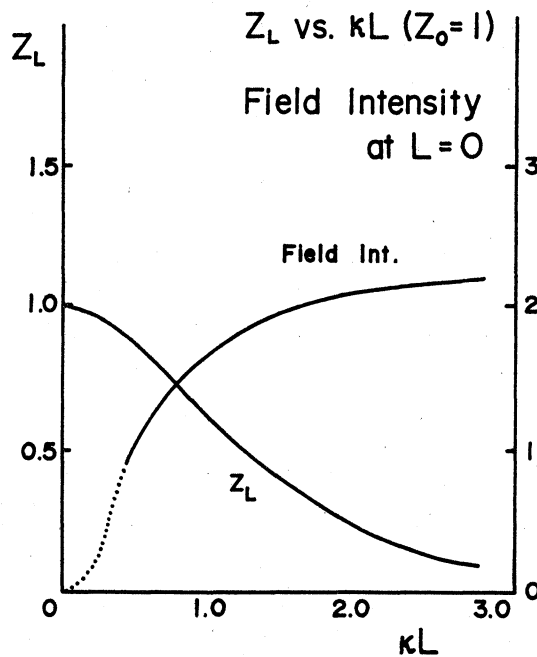


Fig. 2

It becomes possible from the results shown in Fig. 1 to obtain the relation of  $z_L$  vs.  $s_L = \kappa L$  and that of field intensity at the film surface vs.  $s_L$ . The results shown in Fig. 2 indicate that the field intensity, in an arbitrary scale, tends to a finite value as  $z_L$  tends to zero. At  $z_0 = 5$ ,  $z_L = 0.4 \times \Phi_\infty(z_0 = 5) = 0.4 \times 0.26 = 0.104V$  for  $L \simeq \kappa^{-1}$  and  $z_L = 0.4 \times \Phi_\infty(z_0 = 5) \simeq 0.16V$  for  $L \simeq (1/2)\kappa^{-1}$ ; the static potential at the midpoint of NaCl thin film of thickness  $10^{-5}$  cm at  $600^\circ K$  is approximately  $-0.104V$ .

### Impure Case

Consider a film containing divalent metallic impurity. In what follows, the three assumptions will be made; (1) the impurity density  $n_{if}/N \lesssim 1$ ; no saturation of impurity occur, (2) the static potential at the middle of the bulk crystal be positive;  $\Phi_\infty > 0$ , i.e. numbers of positive ion vacancies be solely determined by the presence of positive divalent impurity, and finally (3) numbers of negative ion vacancies be negligibly small;  $n_-/N \simeq 0$ .

Impurity concentration  $\bar{C}$  is defined by the following expression.

$$\bar{C} = \frac{1}{NL} \int_0^L dx(n_{if} + n_{ib}), \quad (18)$$

where  $n_{ib}$  stands for the numbers of impurity-positive ion vacancy pairs. In parallel with Kliewer and Koehler's treatments, one obtains  $n_+$ ,  $n_-$ ,  $n_{if}$ ,  $n_{ib}$  and  $n_B$  subject to the minimization of total free energy of the system. The form of Poisson's equation in this case becomes to be identical to that in the pure crystal;

$$\frac{d^2 z(s)}{ds^2} = \sinh z(s). \quad (19)$$

Local charge density  $\rho(x)$  is  $e(n_{if} + n_- - n_+)$ . Relations to determine  $z_0$ ,  $z_L$  and  $\kappa$  for given  $\bar{C}$  and  $L$  are the followings;

$$\exp[z_0] = A\kappa^{-1} \exp\left[-\frac{F^+}{2kT}\right], \quad (20)$$

$$\kappa L = \zeta' F \left( \sin^{-1} \left\{ \frac{\cosh z_0 - \cosh z_L}{\cosh z_0 - 1} \right\}, \zeta' \right), \quad (21)$$

$$\frac{\kappa^2}{A} = \frac{\bar{C}}{B + \frac{A}{\kappa^2 L} \exp\left[-\frac{F^+}{2kT}\right] \int_0^{\kappa L} \exp[-z(s; z_0, z_L)] ds}, \quad (22)$$

where  $A$ ,  $B$  are constants inherent to the crystals and  $\zeta'$  is equal to  $\sqrt{\frac{2}{1 + \cosh z_L}}$ . Eq. (20) is the relation between  $z_0$  and Debye thickness  $\kappa$  and eq. (21) is derived from  $z = z(s; z_0, z_L)$  with  $s = 0$ . Eq. (18) will result in eq. (22).

As easily seen,  $n_{if}/N$  is proportional to  $\exp[z]$  in which  $z = z(s; z_0, z_L)$  is a solution of Poisson's eq. (19). Fig. 3 shows  $\exp[z]$  vs.  $s (= \kappa_1 z)$ , where  $\kappa_1$  indicates  $\kappa$  for  $z_0 = -1$ .

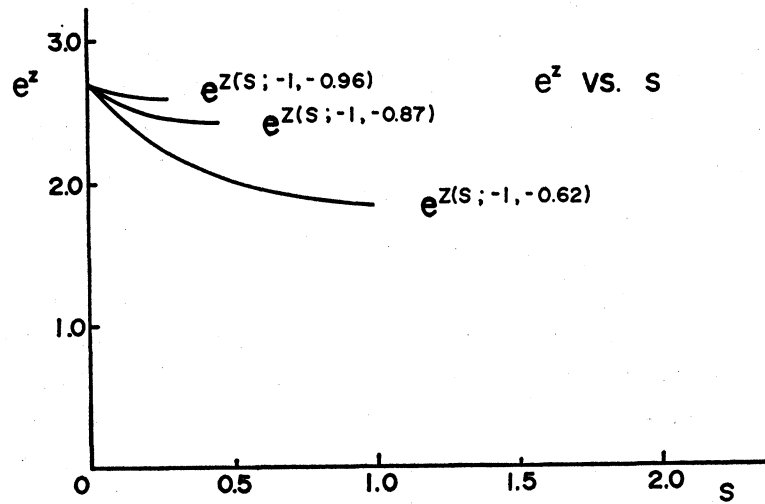


Fig. 3

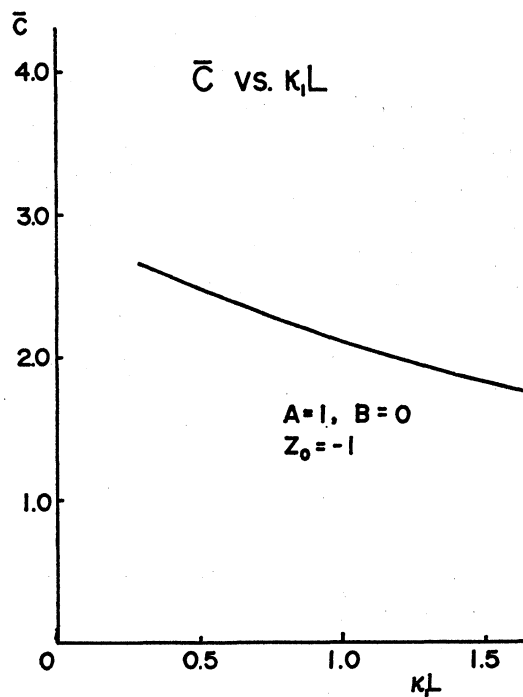


Fig. 4

Here parameters  $z_L$  are  $-0.96$ ,  $-0.87$ ,  $-0.62$ . The relation of  $\bar{C}$  vs  $\kappa_1 L$ , shown in Fig. 4, can be obtained by the help of eq. (22) after evaluating the integral in the denominator. The curve in Fig. 4 tends to the impurity concentration of the bulk crystal the internal potential of which corresponds to  $z_0 = -1$ . In order to find the potential profile inside the film, one obtain  $z_0$  by one of the  $\bar{C}$  vs.  $L$  curves which runs through the point at given  $L$  and  $\bar{C}$ , then determines  $\kappa$  by eq. (20). Finally,  $\Phi(x)$  vs.  $x$  will be found by  $z = z(s; z_0, z_L)$ .

### § 3 Summary

1. In case of pure thin film, an electrostatic potential,  $n_+$  and  $n_-$  do not change appreciably compared to the bulk crystal.

2. In thin films with divalent impurity, the concentration of impurity  $C$  increases with decreasing film thickness. Since the sign of electrostatic potential corresponds to that of  $\Phi_\infty$  of the bulk crystal, an isoelectric temperature may not change.

3. In cases mentioned above, a charge neutrality is not maintained inside the crystal so that there exist excess plus or negative ion vacancies depending on the crystal temperature.

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